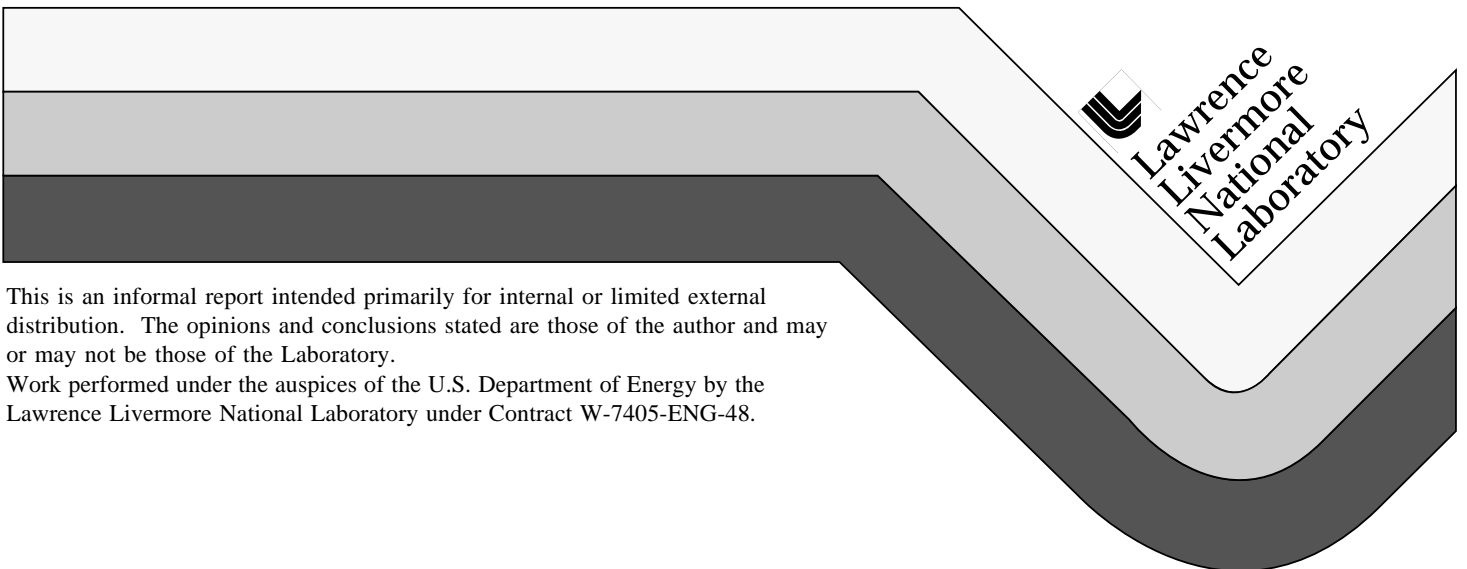


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# Silver Removal Process Development for the MEO Cleanout\*

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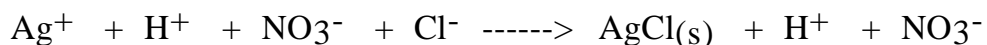
## I. Introduction

The Mediated Electrochemical Oxidation (MEO) system is an aqueous process which treats low-level mixed wastes by oxidizing the organic components of the waste into carbon dioxide and water. As MEO system continues to run, dissolved ash and radionuclides slowly accumulate in the anolyte and must be removed to maintain process efficiency. At such time, all of the anolyte is pumped into a still feed tank, and the silver ions need to be removed before sending the solution to a thin-film evaporator for further concentration (Reference 1). The efficiency of removing silver ions in the solution needs to be high enough such that the residual silver sent to Final Forms would be less than 1% wt. (Reference 2). The purpose of this work is to develop an efficient process to remove silver ions during the MEO cleanout and to demonstrate the capability of centrifugation for separating small silver chloride particles from the solution. This development work includes lab scale experiments and bench scale tests. This report summarizes the results.

## II. Lab Scale Experiments

### A. Chemistry

Hydrochloric acid is an effective reagent to remove silver ions in the anolyte as shown by the chemical reaction below:



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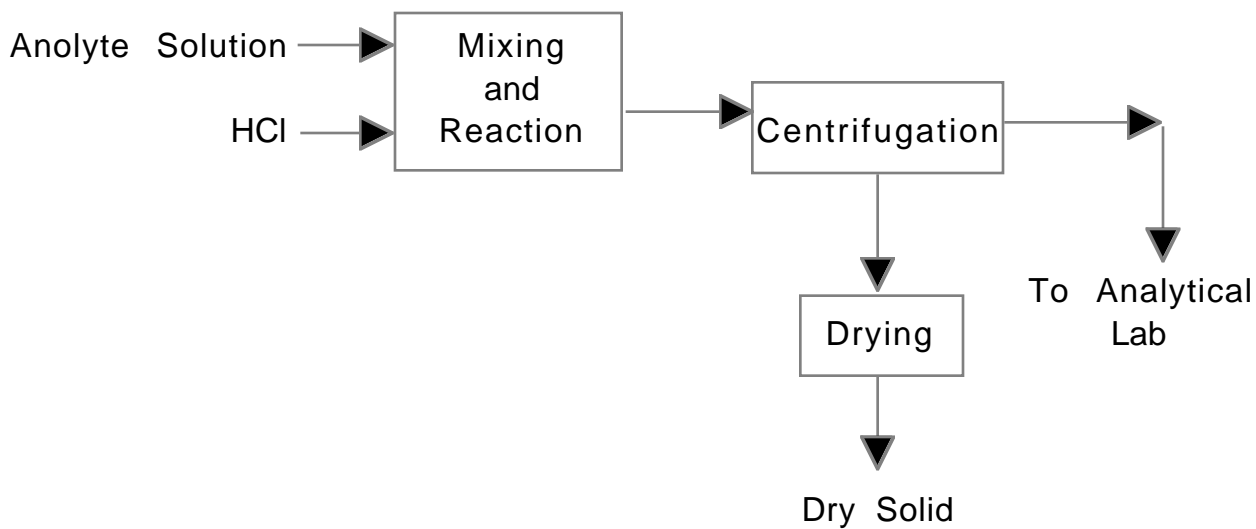
\*This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

The concentrations of silver ions and nitric acid in the anolyte solution are about 0.4 - 0.5 M and 8 M, respectively. The concentration of dissolved ash in the anolyte before a cleanout is required is about 10%wt.

## B. Lab Scale Experiments

Fig. 1 describes the procedure for lab scale experiments.

Fig. 1 Lab Scale Silver Removal Process

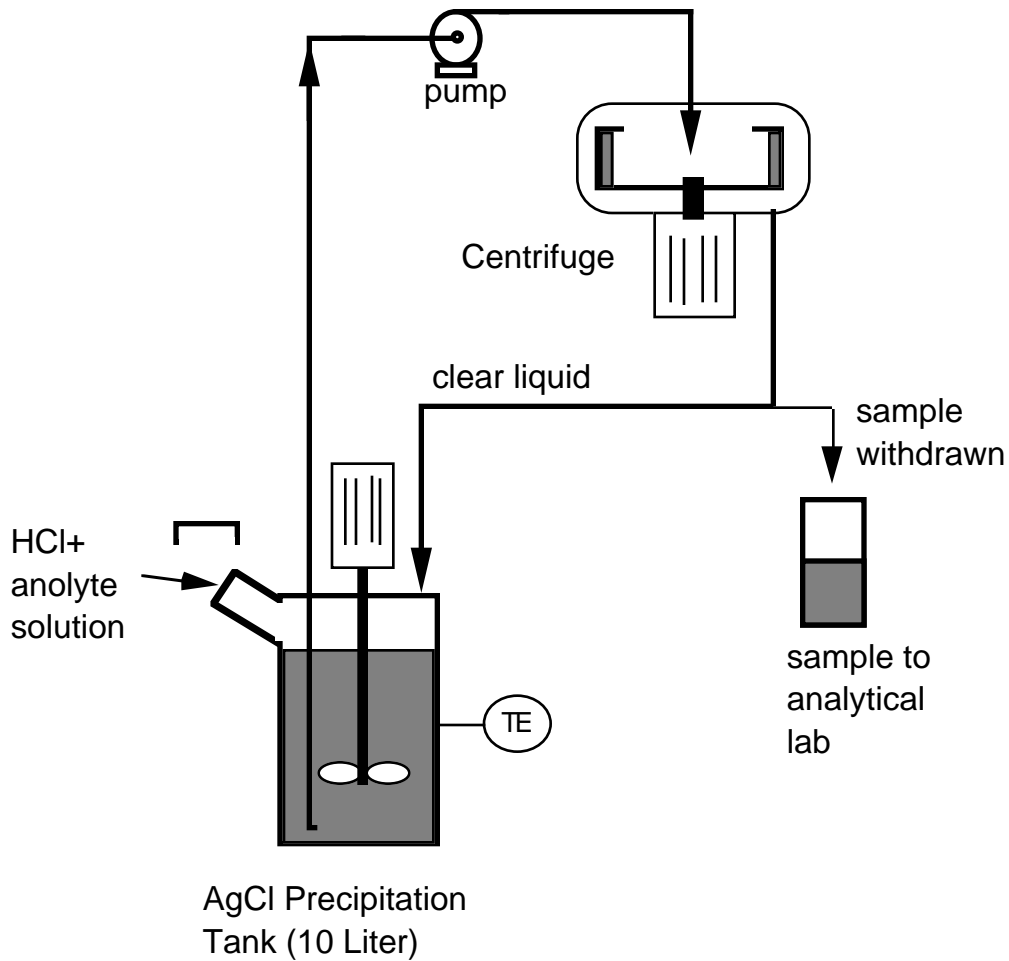


Anolyte solution 50 CC was heated up to about 60°C under mixing before adding hydrochloric acid to the solution. The product, silver chloride, formed and precipitated. Mixing speed was maintained at about 400 rpm to ensure a "just suspended" condition. The solution was mixed for 30 minutes before centrifuging and separating the silver chloride solids out from the solution. The solids were dried in an oven at 80°C overnight. The solution was sent to Analytical Laboratory for analysis of residual silver ions. The removal efficiencies were estimated based on the concentrations of silver ions before and after the reaction.

### III. Bench Scale Unit Description and Operation Procedure

As part of the process development, a bench scale unit was built to test the scaling effect of silver removal process. This unit utilized the existing equipment from bench scale silver recovery system (Reference 3). Fig. 2 shows the bench scale silver removal process.

Fig. 2 Bench Scale Ag Removal Unit



The bench scale unit and its operation procedure are described as follows:

## 1. Precipitation Tank

The precipitation tank was made of glass with volume of 10 liters. It was a cylindrical vat with a cover to prevent reaction medium from spilling out. A heating plate was used to heat up the solution to a desirable temperature range 50 to 60°C. The solution temperatures were monitored by a thermometer. The transparent nature of the glass also allowed us to observe and adjust mixing conditions.

## 2. Mixer

The mixing speed was maintained at about 400 rpm by a Variac to achieve a good mixing. The impeller width was 3 inch. The shaft was made of stainless steel to avoid corrosion.

## 3. Pump

A peristaltic pump was used to transfer slurry from the precipitation tank to a centrifuge. Pump capacities were from 1 to 5 liters per minute.

## 4. Centrifuge

The bowl volume of the centrifuge is 2 liters. The centrifuge's g-value is 500 and revolution is 1725 rpm.. The bowl was made of stainless steel.

## 5. Sample Bottle

Small sample bottles were used to take samples from the clear liquid return line. The samples were sent to Analytical Laboratory for analysis.

## 6. Tubing and Fittings

All the tubing is made of flexible polymers (Tygon) for the ease of operation. Fittings are made of Teflon and Kyner.

Anolyte solution 4000 g (3037 CC) was poured into the precipitation tank under mixing. The solution was then heated up to a desirable temperature range by a heating plate before adding HCl into the tank. Precisely measured amounts of hydrochloric acid were added in for about 45 seconds. Reaction was very fast and the product silver chloride formed. A thermometer was used to monitor the solution temperatures during the course of reaction.

After a desired reaction time of 30 minutes was reached, the solution slurry was transferred to a centrifuge by a peristaltic pump at a rate of 2.5 liters/min. for solid-liquid separation. The solution recycled back to the tank and solids stayed in the centrifuge bowl. Several recycle passes were needed in order to achieve a good separation. Samples were taken from the clear liquid return line and then sent to the Analytical Laboratory for analysis of residual silver ions.

Table 1 shows the scales of lab scale unit, bench-scale unit and MWMF scale.

Table 1

<u>System</u>	<u>Amounts of Anolyte Treated</u>	<u>Location</u>	<u>Scale ratio</u>
Lab Scale	50 CC	B-241	1
Bench-Scale	3.0 liters	B-161	60
Pilot-Plant	210 liters	MWMF	4200

Table 1 shows that scale up ratios 60 from lab-scale to bench scale and 70 from bench scale to MWMF pilot scale, respectively. A successful operation of the bench scale unit would provide important design information to the MWMF pilot scale unit.

#### **IV. Test Results**

##### **1. Removal Efficiencies at 1.0X HCl Stoichiometry**

Since silver chloride is not soluble in anolyte solution, the stoichiometry of HCl required for removing silver ions from the solution should be close to 1. Therefore a theoretical amount of HCl was used in the beginning to test the removal efficiencies for the lab scale and bench scale unit. The results are shown in Table 2.

Table 2

System	HCl Stoichi.	Ag Conc., M		Removal Eff.	Residual AgCl in Final Form**
		Before	After		
Lab-scale	1.0X HCl	0.4926	6.14E-03	98.75%	0.88%wt.
BSP-1	1.0X HCl	0.4056	1.78E-03*	99.56%	0.36%wt.

\* Sample taken at 21 minutes after starting the centrifuge or 10 recycle passes.

\*\* Anolyte solution assumed to contain about 10%wt. dissolved ash before MEO cleanout.

Table 2 shows that, from both lab-scale and bench scale, silver removal efficiencies are good at 1.0X HCl stoichiometry. The residual silver in the anolyte after the silver removal process will go to Final Forms with concentrations less than 1%wt.

## 2. Removal Efficiencies With Excess HCl

To test the silver removal efficiencies with excess HCl, two tests, namely, BSP-2 and BSP-3 were conducted and the results are tabulated in Table 3.

Table 3

Test	HCl Stoichi.	Ag Conc., M		Removal Eff.	Residual AgCl in Final Form
		Before	After		
BSP-2	1.05X HCl (5% excess)	0.4056	4.15E-06	99.999%	0.0026%wt.
BSP-3	1.005X HCl (0.5% excess)	0.4056	5.04E-05	99.990%	0.028%wt.

Table 3 shows that excellent silver removing efficiencies were achieved with a slightly excess HCl. The result from test number BSP-3 indicates that the residual silver chloride going to Final Form can be as low as 0.028%wt with 0.5% excess HCl.

### 3. Time of Centrifugation

One of the objectives for the bench scale test is to determine how efficient a centrifuge can be when used for separating silver chloride from anolyte solution. Many samples were taken for the test BSP-3 during the centrifugation and the results are shown in Table 4.

Table 4 BSP-3 Centrifuge

<u>Time of Centrifuge</u>	<u>Recycle Passes</u>	<u>Ag ion Conc., M</u>	<u>Total Ag * Conc., M</u>	<u>Residual AgCl in Final Form</u>
7 min.	3.5	5.04E-05	19.10E-05	280 ppm (0.028%)
14	7.0	5.07E-05	9.89E-05	144 ppm
21	10.5	4.64E-05	9.09E-05	132 ppm
58	29.0	3.34E-05	6.53E-05	95 ppm
70	35.0	3.20E-05	4.64E-05	68 ppm

\* Total Ag includes silver ions and tiny AgCl particles suspended in solution.

Table 4 shows that centrifugation is very effective for separating AgCl particles out from the solution. The residuals AgCl concentration is only 0.00019 M after 3.5 recycle passes.

### 4. Optimal Condition

Fig. 3 shows the Ag content in the residual solids sent to Final Forms. Overlaid on the same plot is the resulting pH of the waste water distillate sent to Water Treatment. As more excess HCl is used in the clean-out operation the Ag content of the solid residues sent to Final Forms is reduced, but the pH of the resulting distillate water sent to Water Treatment is also lowered. If the distillate water pH gets below about 2 the resulting salt content after neutralization is too high to directly sewer and the water must be treated to remove the salt. It is therefore desirable to use no more than 0.02% excess HCl (pH > 3 waste water) unless the resulting Ag level of approximately 0.35% wt in the residue solids is too high for Final Forms to handle comfortably. In that event the HCl concentration can be increased to lower the Ag with the resulting penalty that Water Treatment will need to reduce the salt content of the water before it can be sewered. This is not a very severe penalty since cleanouts occur at intervals of greater than 312 hours operating time at the maximum solids

content in the feed of 5% of the organics loading. This is determined as follows:

$$t = (60\text{L})(1.3\text{kg/L})(0.1\text{kg solid/kg anolyte})(20\text{kg organic/kg solid}) / (0.5\text{kg/h}) = 312 \text{ hr}$$

vol anolyte = 60L (estimated)  
 anolyte density = 1.3 (assume 10M)  
 solids loading of anolyte = 0.1  
 20kg organic/kg solid = max loading of dirt in feed  
 0.5kg/h = max. organic feed rate

For cleaner feeds, or if dirty anolyte is integrated up to 400 L in the still feed tanks, this time can be extended into the thousands of hours.

Over the same 312 hrs, approximately 156L of water will be produced at a minimum (10x this amount could be produced for highly aqueous feeds). The 60L of anolyte, when distilled to 13M HNO<sub>3</sub> and water will yield approximate 13L of waste water. Thus the yield of low pH water will be at most 8.3% of the total waste water produced by MEO. In practice, this will be much lower, since most feeds will not possess all of the extreme properties assumed above.

The pH of the waste water is determined as follows:

$$\text{pH} = -\text{Log}\{(0.5\text{M-Ag/L})(1\text{M HCl/M-Ag})(0.005 \text{ excess}) / (0.22 \text{ distillate/anolyte ratio})\}$$

$$\text{pH} = 1.94$$

$$\begin{aligned} \text{anolyte Ag content} &= 0.5\text{M-Ag/L} \\ \text{excess HCl used} &= 0.5\% \text{ (assumed for example)} \\ \text{waste water to anolyte ratio} &= 0.22 \text{ (assume 10M anolyte)} \end{aligned}$$

The results of this computation for various excess quantities of HCl are shown in Fig's 3 & 4. The use of Fig's 3 & 4 allow the operator to select the output of Ag to Final Forms and the resulting pH of the waste water, depending upon the requirements of each for the specific waste stream.

## 5. Reagent Requirement

The only reagent required for the silver removal process is HCl which is inexpensive.

## V. Conclusions

The silver removal process during the MEO cleanout has been successfully developed in the lab-scale and bench scale. High silver removal efficiency has been achieved using HCl as the precipitating reagent. Centrifugation has been demonstrated as an excellent way to separate AgCl particles from the anolyte solution. Hydrochloric acid is the only reagent required for the process. The trade-off between Ag going to Final Forms in the solid residues and HCl going into the waste water has been determined and data is provided to make a quantitative selection. The results from this process development provide a very useful information for the design and operation of the MEO process.

**Ag cleanout data for MEO,  
assuming 10% dissolved solid  
loading in anolyte at cleanout time.**

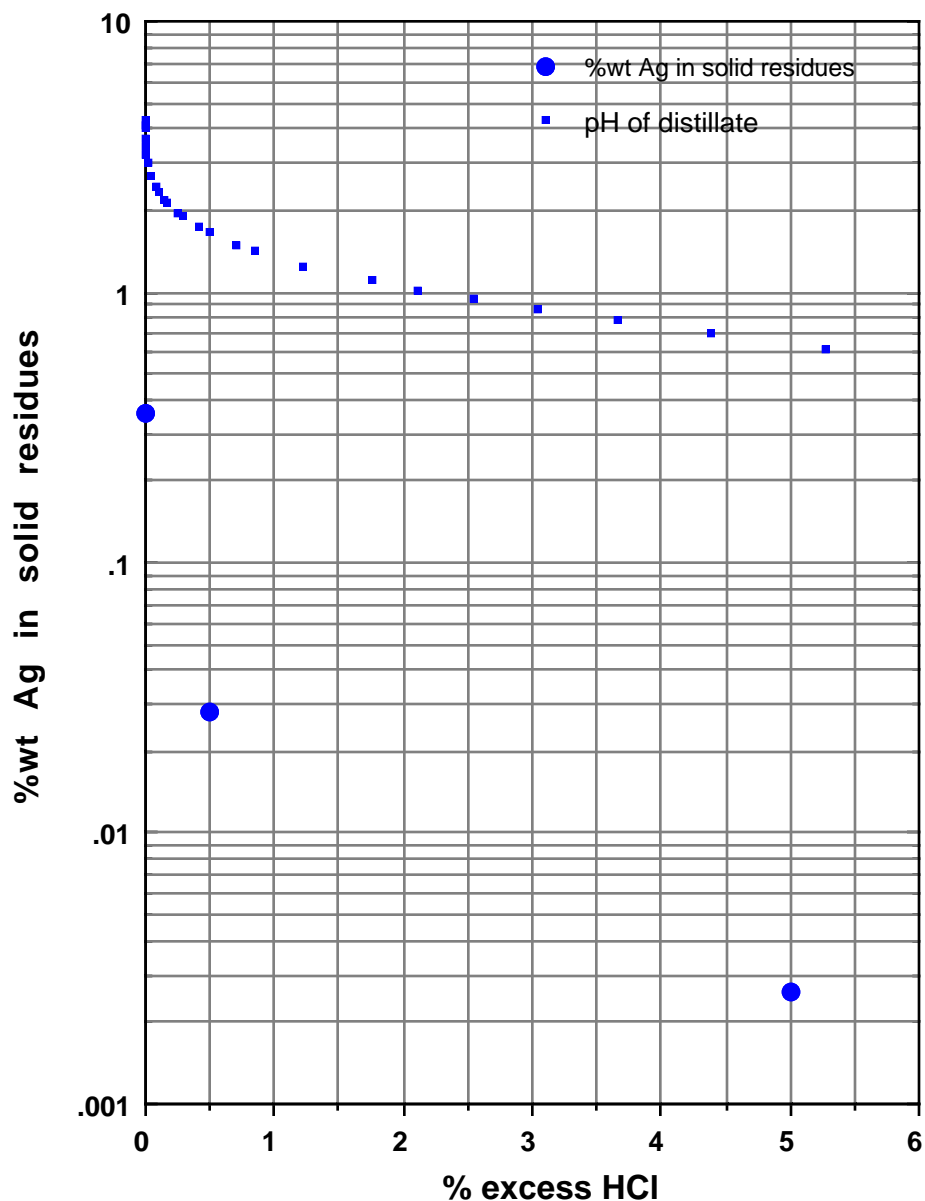


Fig. 3 - Showing the residual silver content in solids sent to Final Forms as a function of the excess HCl used in the clean-out operation. Also shown is the estimated pH of the resulting water distillate sent to Water Treatment as a result of the HCl (assume 0.5M Ag to remove). The estimate of pH assumes anolyte of 10M HNO<sub>3</sub> split into pure water and 13M HNO<sub>3</sub> with all HCl going to the water phase. The water volume is about 22% of the anolyte original anolyte.

Ag cleanout data for MEO,  
assuming 10% dissolved solid  
loading in anolyte at cleanout time.

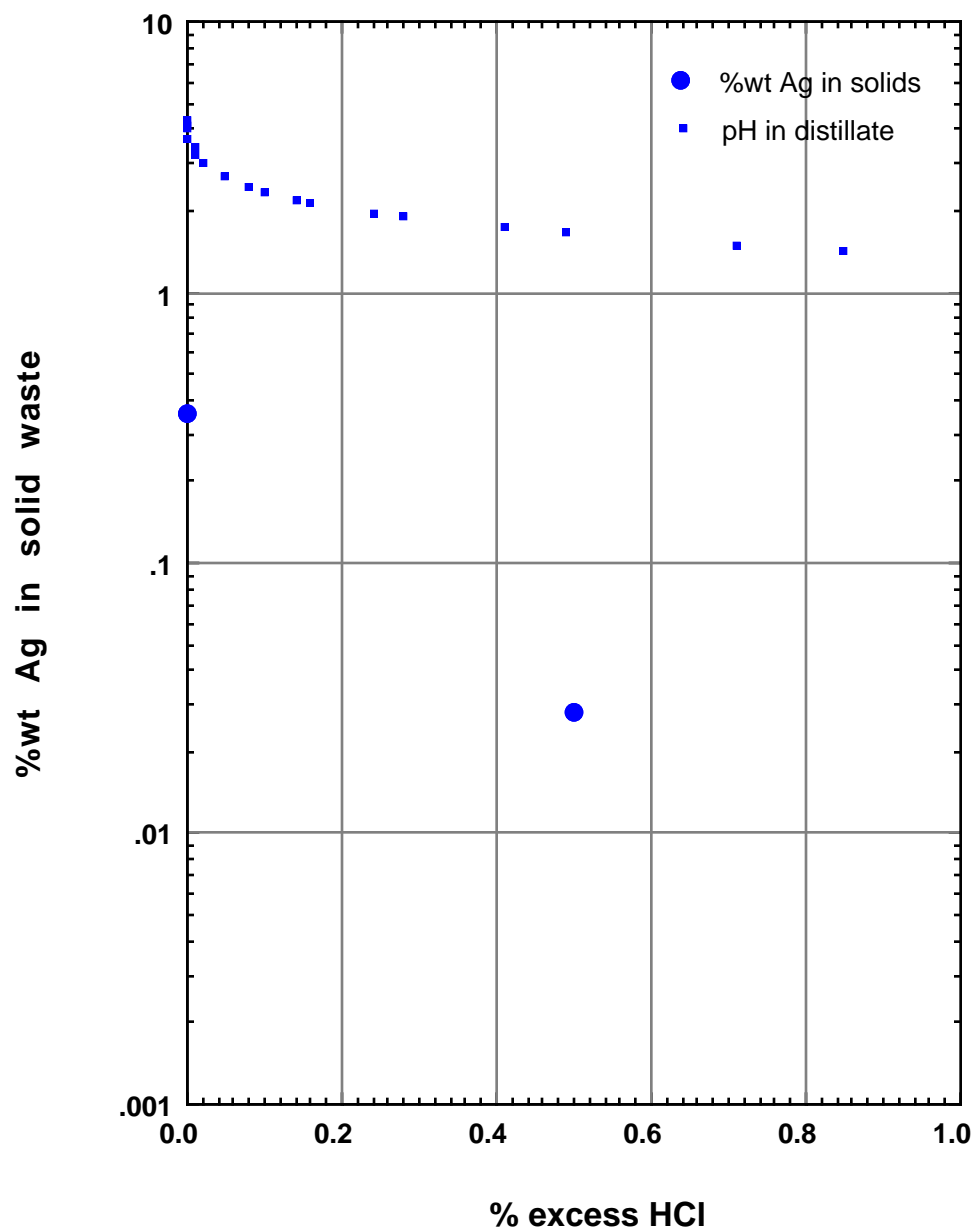


Fig. 4 - Same as Fig. 3 except scale expanded to show the 0 to 1% excess HCl region.

## **References**

1. "Mixed Waste Management Facility Conceptual Design Report", UCRL-PROP-116761, L-17293-1, April, 1994.
2. Per Conversation with Bob Hopper in June 1995.
3. Peter C. Hsu, Zoher Chiba, and Bruce Schumacher, "Bench Scale Silver Recovery for MEO System", L-19707-1, WBS 1.5.1.3.1, June 1995.